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INVESTIGATION OF SOME PHYSICAL PROPERTIES OF CdS FILMS AT DIFFERENT Mn INCORPORATION

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ABSTRACT

CdS and Mn incorporated CdS:Mn (%10, %30) films were deposited onto glass substrates at 275±5°C by a low cost and simple ultrasonic spray pyrolysis technique and annealed at 500°C during 3 hours at air atmosphere. Optical, electrical and surface properties of the films were investigated in order to determine of application potential on photovoltaic solar cells. Spectroscopic Ellipsometry and UV/VIS spectrophotometry techniques were used to determine of film thicknesses and some optical properties. Band gaps of CdS and CdS:Mn films were identified using optical method as 2.14 eV, 2,24eV and 2.16 eV, respectively. It was determined that the refractive indices values of the films changed between 1.73-1.80 and extinction coefficient values remain constant around 0.10. Surface morphologies and roughness values of the films were investigated by Atomic Force Microscopy. Also, electrical resistivities of all films determined by four point probe technique between 5.5×10^4 - 4.8×10^5 Ωcm.

Keywords: *Ultrasonic Spray Pyrolysis, CdS, Mn, Spectroscopic Ellipsometry, Atomic Force Microscopy*

FARKLI ORANLARDA Mn İÇEREN CdS FİLMLERİNİN BAZI FİZİKSEL ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

CdS ve farklı oranlarda (%10, %30) mangan (Mn) katılmış CdS:Mn filmleri uygulaması kolay ve ekonomik olmasıyla dikkat çeken ultrasonik kimyasal püskürtme (UKP) yöntemi ile 275±5°C taban sıcaklığında üretilmiş ve 3 saat süreyle 500°C sıcaklıkta tavlama işlemine tabi tutulmuştur. Tüm filmlerin fotovoltaik güneş hücrelerinde kullanım potansiyelini araştırmak amacıyla optik, elektrik ve yüzey özellikleri incelenmiştir. Elde edilen filmlerin kalınlıkları ve bazı optik özelliklerinin belirlenmesi için Spektroskopik Elipsometri (SE) ve UV/VIS Spektroskopi teknikleri kullanılmıştır. Optik metot kullanılarak ham ve Mn katılmış CdS:Mn filmlerin optik bant aralıkları sırası ile 2.14 eV, 2,24eV ve 2.16 eV olarak belirlenmiştir. Elde edilen filmlerin kırılma indisi değerlerinin 1.73-1.80 aralığında değiştiği ve sönüm katsayısı değerlerinin ise 0.10 civarında sabit kaldığı saptanmıştır. Yüzey morfolojileri ve yüzey pürüzlülük değerleri atomik kuvvet mikroskobu kullanılarak incelenmiş ve dört uç metodu ile CdS ve CdS:Mn filmlerinin elektriksel özdirençlerinin 5.5×10^4 - 4.8×10^5 Ωcm aralığında değiştiği belirlenmiştir.

Anahtar Kelimeler: *Ultrasonik Kimyasal Püskürtme, CdS, Mn, Spektroskopik Elipsometre, Atomik Kuvvet Mikroskobu*

1. INTRODUCTION

CdS is a technologically important II-VI semiconductor material, especially for photovoltaic solar cells and optoelectronics. It has been used in various applications such as window material for solar cell, optical filter, photodetectors and optoelectronic devices [1-5]. The production of CdS thin films have been investigated by different techniques such as chemical bath deposition, sputtering, electrodeposition, spray pyrolysis and thermal evaporation [6-9], etc. Among these, spray pyrolysis is the most promising technique to produce CdS films for solar cell applications onto large areas easily without the need of vacuum. In this technique, properties of the films depend on many parameters such as flow rate, substrate temperature, doping ratio etc. Therefore, production parameters should be optimized for each application in order produce effective materials and/or thermal annealing process is applied to produced films. However, incorporation of different elements such as Mn [10-17], Fe [18], Co [19], Cu [20] into CdS film is the most promising method in recent years. Incorporation is important for semiconductors, which plays a critical role in tuning their optical and electrical properties in solar cells [21- 23]. In this work, optical, surface and electrical properties of thermally annealed at 500°C CdS and CdS:Mn films produced by ultrasonic spray pyrolysis (USP) technique have been characterized using SE, UV/VIS spectrophotometer, AFM and four point probe technique and also the application potential of them for solar cell devices have been reported.

2. MATERIAL AND METHOD

CdS and CdS:Mn (at 10 and 30 %) films were produced by USP technique onto heated microscope glass (Objekttrager, 10x10 mm^2) substrates which first ultrasonically cleaned with ethanol and de-ionized water. Substrate temperature was adjusted at 275±5°C and controlled using an iron-constantan thermocouple. Totally 50 cc solution was sprayed onto substrates. The solution flow rate was kept at 2.5 cc min^{-1} and controlled by a flowmeter during 20 min. This liquid solution was mixed by magnetic stirrer both before and during deposition. Spraying solution consists of (0.01 M) $CdCl_2.2H_2O$, $CS(NH_2)_2$ and $MnCl_2$. Compressed air (1bar) was used as the carrier gas and was continued for a further 10 minutes after production process to avoid sudden temperature changes. After deposition, produced films were allowed to cool down to room temperature. Thermal annealing were applied to produced films at 500°C during 3 hours and then taken out for further characterization. The samples are labeled as CM0, CM1 and CM3 depending on the increasing volume percent of Mn source in the $Cd_{1-x}Mn_xS$ spraying solution (x= 0; 10; 30 %). The thicknesses and some optical parameters of the films were determined by a PHE 102 Spectroscopic Ellipsometer. Optical measurements were performed by Shimadzu-SolidSpec-3700 UV-VIS-NIR Spectrophotometer in the wavelength range of 300-800 nm. Surface characteristics of the films were investigated by Park System XE 70 model Atomic Force Microscope. The measurements were taken in non-contact mode, ~300 kHz frequency and 2 Hz scan rate in air at room temperature. Root mean square (rms, R_q) and average (R_a) roughness values were obtained using XEI Version 1.7.1 software. All the images were taken from an area of 5x5 μm^2, and the roughness values belong to whole scanned area. Also, the electrical resistivity measurements were done using four point probe system.

3. RESULT AND DISCUSSION

SE is an efficient technique to analyze the optical properties and microstructure of the films which is used to polarized light to characterize thin film and bulk materials. In SE measurements, Ψ and Δ spectra are recorded at each wavelength and angle of incidence [24]. These two parameters are related to the optical and structural properties of the sample through the following expression [25]

$$\rho = \frac{R_p}{R_s} = \tan(\psi)\, e^{i\Delta},$$

where R_p and R_s symbolize the complex reflection coefficients for the light polarized parallel *(p)* and perpendicular *(s)* to the plane of incidence, respectively. *Δ,* reflects the change in the phase difference between the incident and reflected waves for respectively p-polarized and s-polarized components. Ψ describes the orientation of the ellipse and tanΨ is the absolute value of R_p/R_s [26-27]. In this work, spectroscopic ellipsometry (SE) was used to determine the thicknesses and optical constants (refractive index and extinction coefficient) of the films. Also, Cauchy model, which is suitable for semiconductors, was used to extract the optical constants of the CdS thin films. The following formulas were used to define the refractive index (n) and extinction coefficient (k) of the Cauchy material;

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$$

$$k(\lambda) = A_k e^{B_k(E-E_b)}$$

where A_n, B_n, C_n, A_k and B_k are the model parameters [28-30]. For these reason, the investigation of the CdS and CdS:Mn films were performed for Δ data at 75° in the wavelength range of 1200-1400 nm in step 10 nm. SE spectra of CdS films are given in Fig 1. A good fit was found between experimental and theoretical values. However, there are some deviations in these values which probably resulted from the surface morphology, grain boundaries and back reflection from glass substrates. The thicknesses and ellipsometric parameters of CdS and CdS:Mn films are given in Table 1. It was seen that the thickness of the films decreased with the incorporation of Mn in the spraying solution. Also, annealing may be caused the decreasing of the thickness of the films due to the good packing.

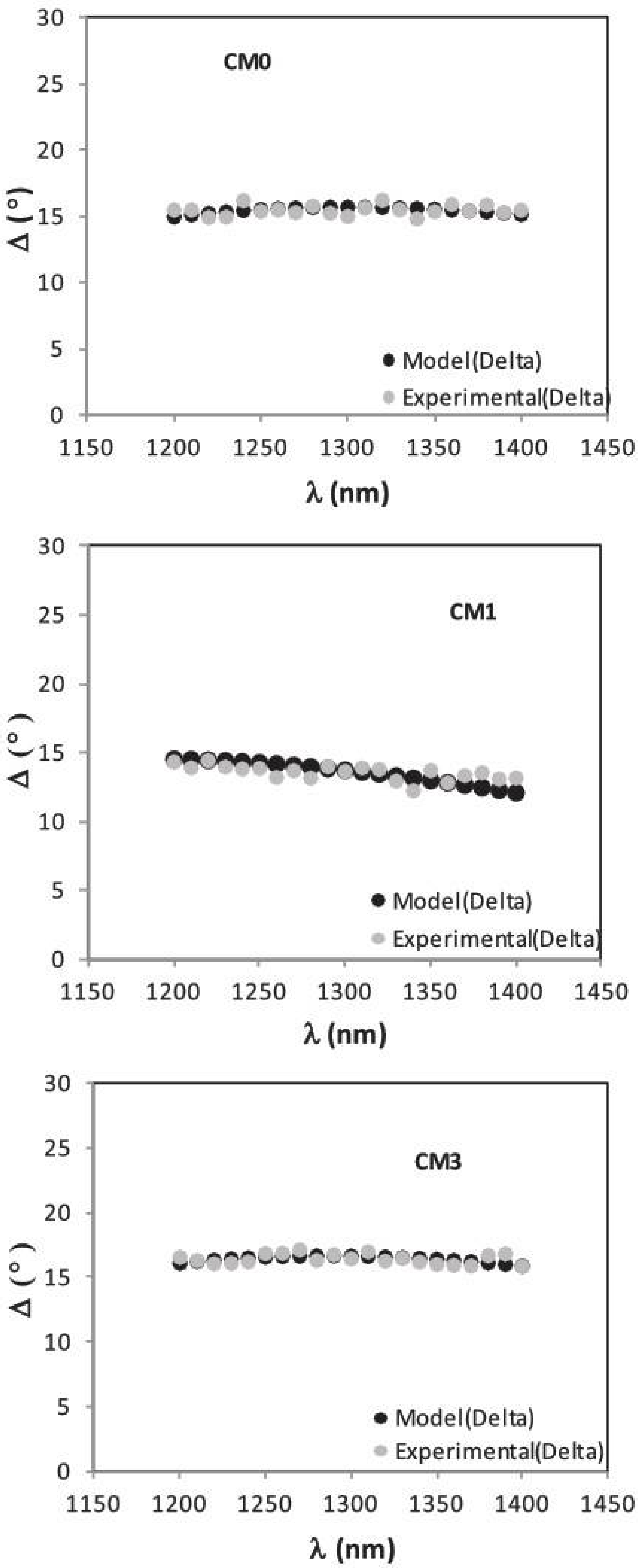
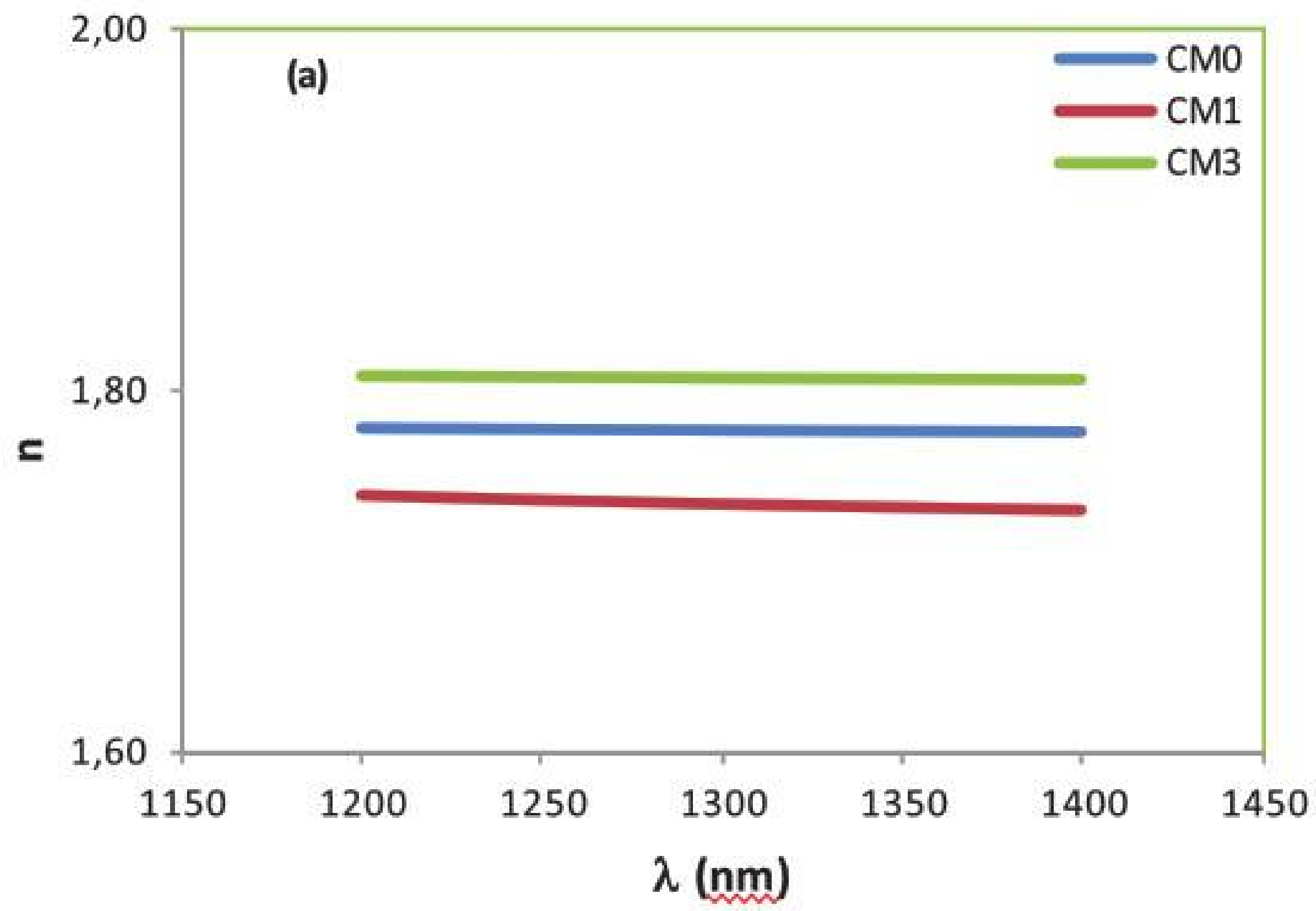


Figure 1. Δ spectra of CdS and CdS:Mn films.

Table 1. The thickness and SE parameters of CdS and CdS:Mn thin films

Film	Thickness (nm)	A_n	B_n $(nm)^2$	C_n $(nm)^4$	A_k	B_k $(eV)^{-1}$	MSE	E_g (eV)
CM0	383	1.77	0.004	0.008	0.46	1.02	0.19	2.14
CM1	285	1.72	0.008	0.026	0.43	1.02	0.40	2.24
CM3	294	1.80	0.005	0.008	0.46	1.03	0.14	2.16

Refractive index n (λ) and extinction coefficient k (λ) spectra of the CdS and CdS:Mn films are shown in Fig. 2 a and b, respectively. In these figures, it is determined that the CM0 film has an average refractive index value in all annealed films at 500 °C. However, it can be said that the 10% Mn incorporation (CM1) was little decreased the refractive index of annealed films while 30% (CM3) little increased. This is may be attributed the light interaction with electrons of the sample and/or surface characteristics of the annealed CdS and CdS:Mn films.



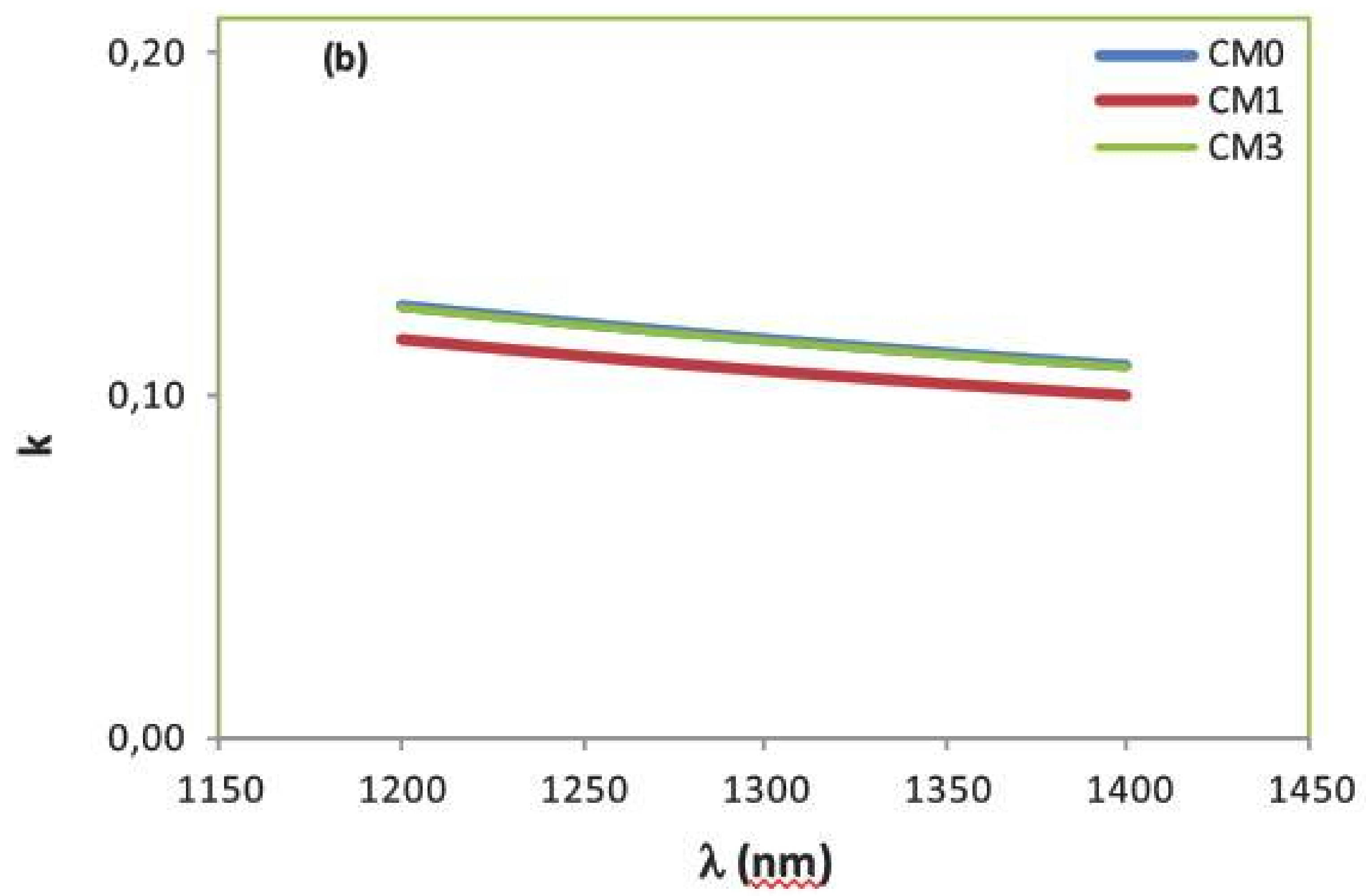


Figure 2. (a) Refractive index spectra (b) extinction coefficient spectra of CdS and CdS:Mn films.

The extinction coefficient of a material is related to its absorption characteristic. So, at long wavelengths films should have low absorption and low *k* values. It is also seen from the Fig. 1 b, the extinction coefficient values is little decreased for CM1 film while CM1 and CM3 films almost same. Besides, it can be said that these values are the same due to this limitations.

Absorbance spectra of CdS and CdS:Mn films, measured in the wavelengths between 300-800 nm, are given in Fig. 3. As seen from Fig. 3, CM0 films have low absorbance value in all samples. Continuity has been determined in the absorption spectra of CM0 film while CM1 and CM3 have characteristic band edge of CdS.

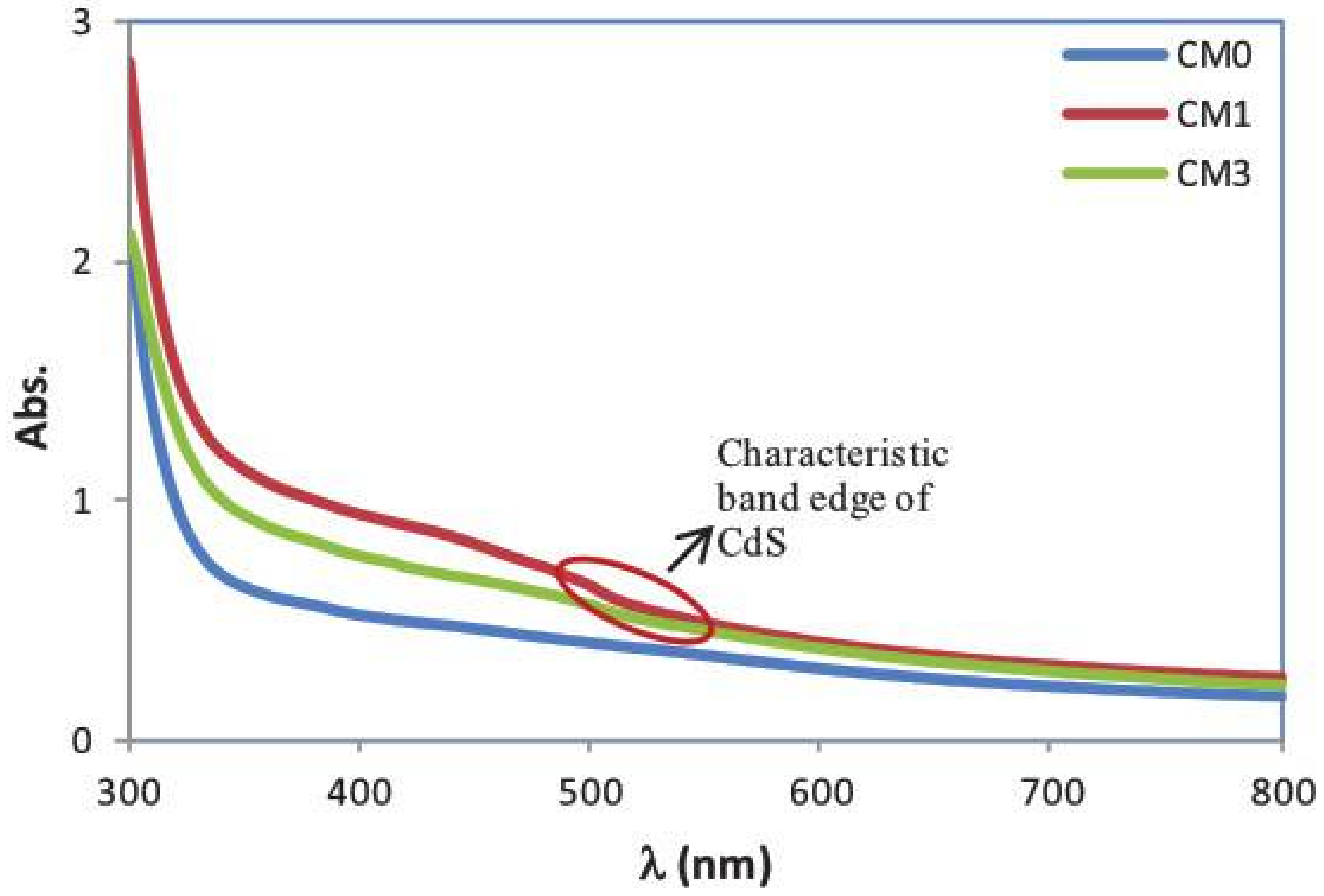
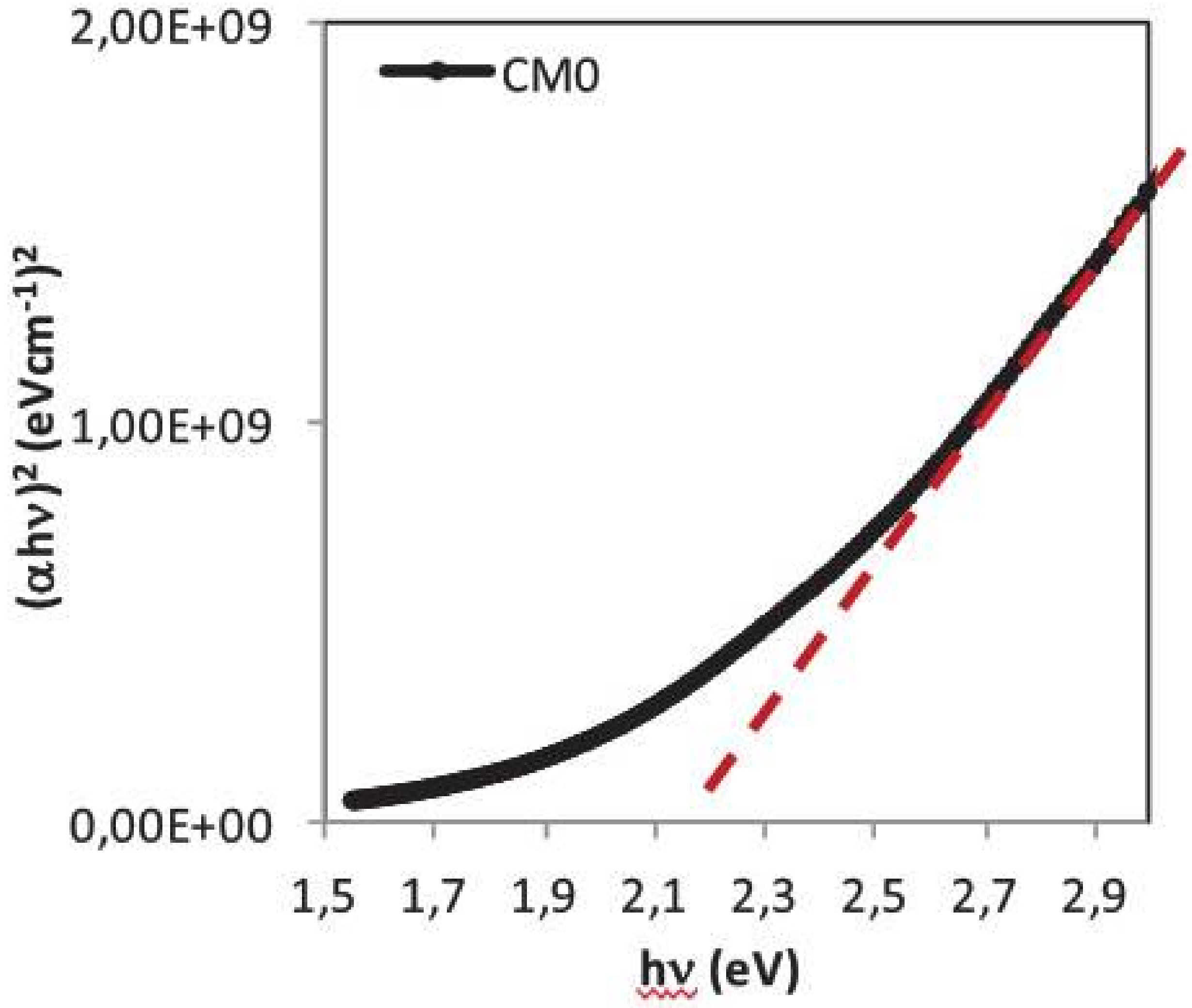
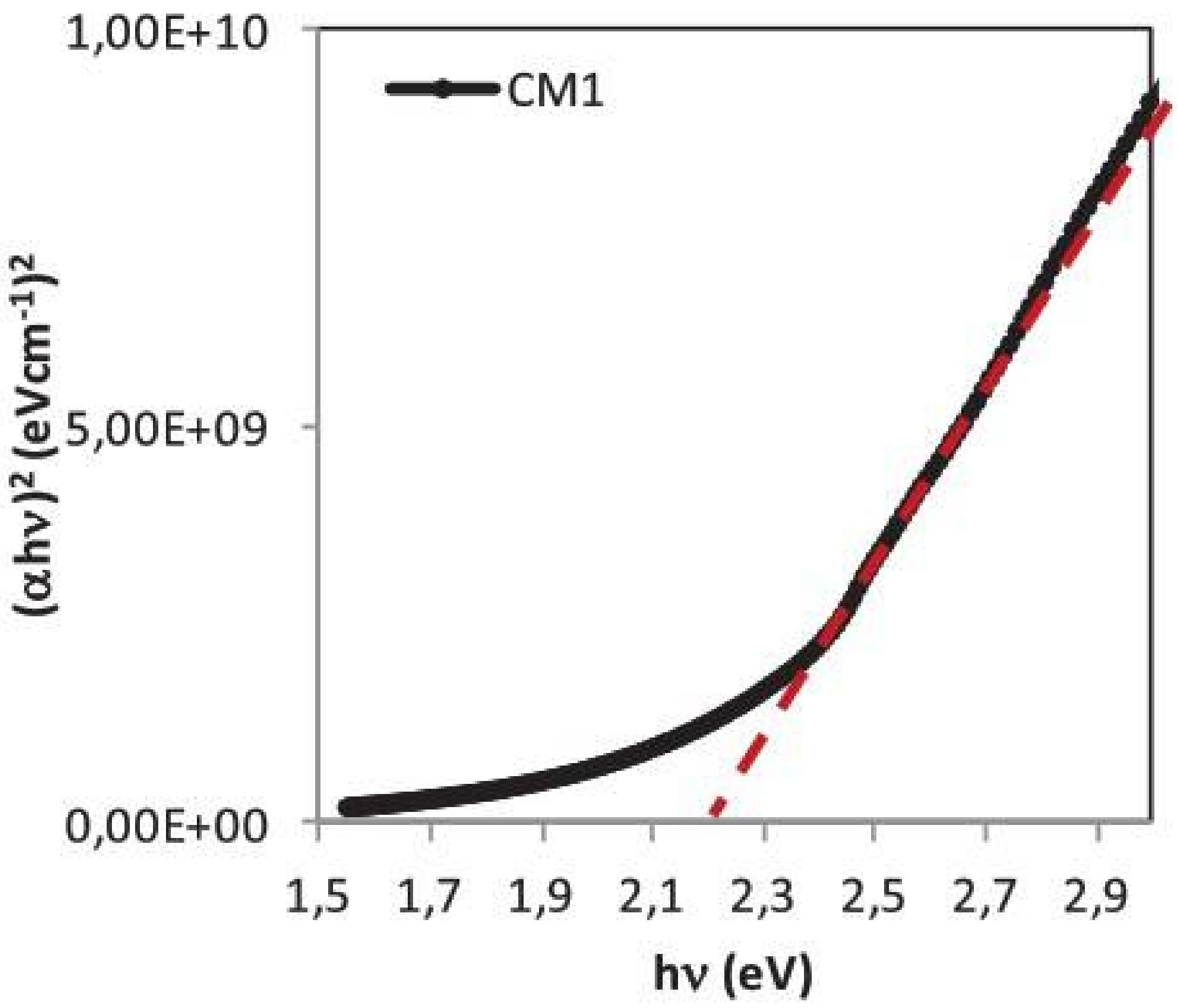


Figure 3. Absorbance spectra of CdS and CdS:Mn thin films

The optical band gaps of the CdS and CdS:Mn films have been determined using the optical method. In this method, the band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ to $(\alpha h\nu)^2 = 0$. The band gap values obtained from these plots are given in Table1. It has been determined that all films have direct band gaps. It has been seen that the optical band gap of the CM1 films increases and CM3 almost same with CM0 films. Also, It is seen that the band gap values of CdS film is under the literature values [31] which can be attributed the crystallinity level of the films.


2,00E+09
1,00E+09
0,00E+00
CM0
(αhν)² (eVcm⁻¹)²
1,5 1,7 1,9 2,1 2,3 2,5 2,7 2,9
hν (eV)


1,00E+10
5,00E+09
0,00E+00
CM1
(αhν)² (eVcm⁻¹)²
1,5 1,7 1,9 2,1 2,3 2,5 2,7 2,9
hν (eV)

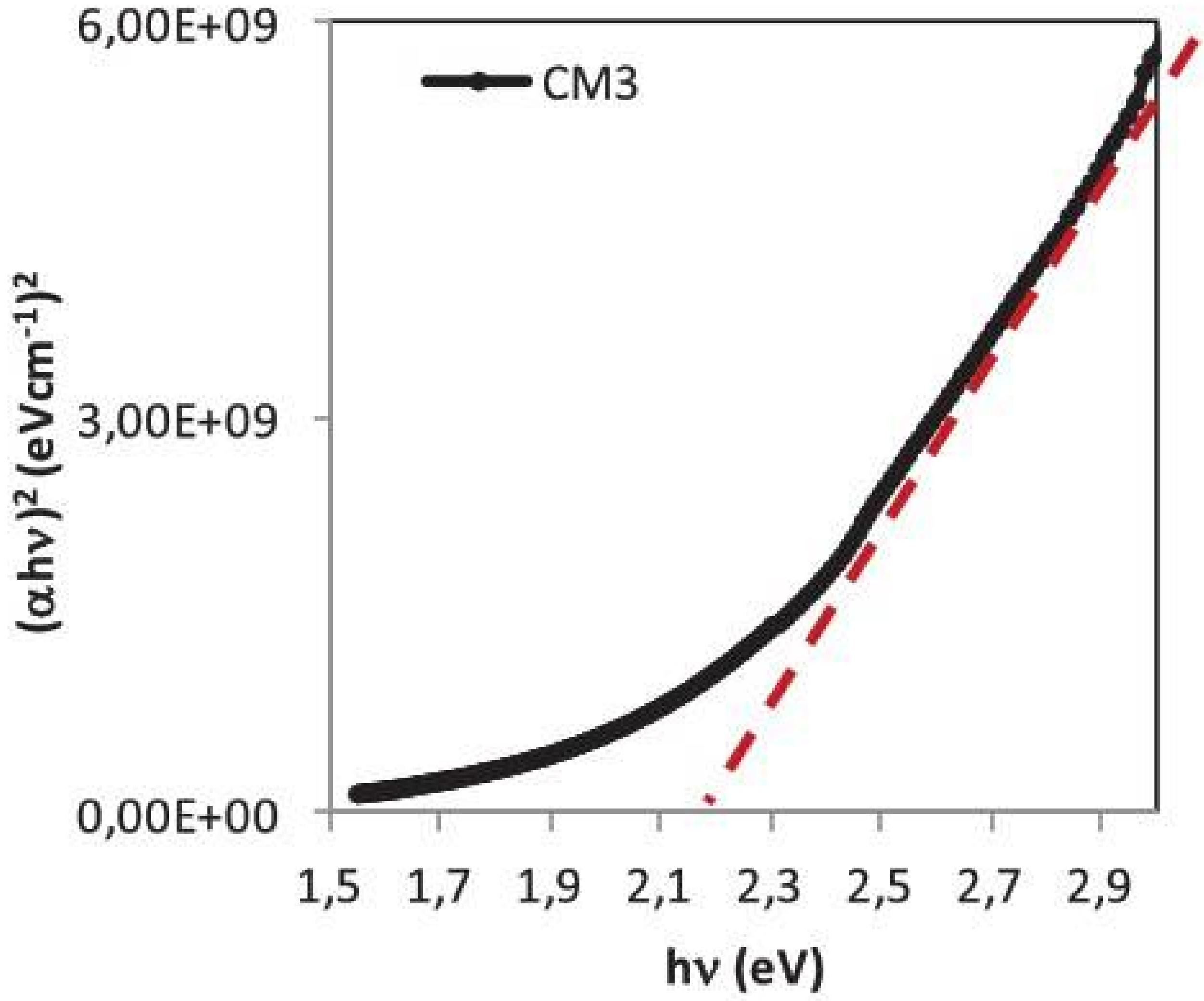


Figure 4. $(\alpha h\nu)^2 \sim (h\nu)$ variations of CdS and CdS:Mn films

AFM images of annealed CdS and CdS:Mn films are shown in Fig. 5. The 5µ x 5µ images are utilized for measuring the surface roughness of the film. Also, Rq (root mean square), Ra (average) and Rpv (peak-to-valley height) roughness values of the film was examined. The roughness values of the annealed CdS and CdS:Mn films are shown in Table 2.

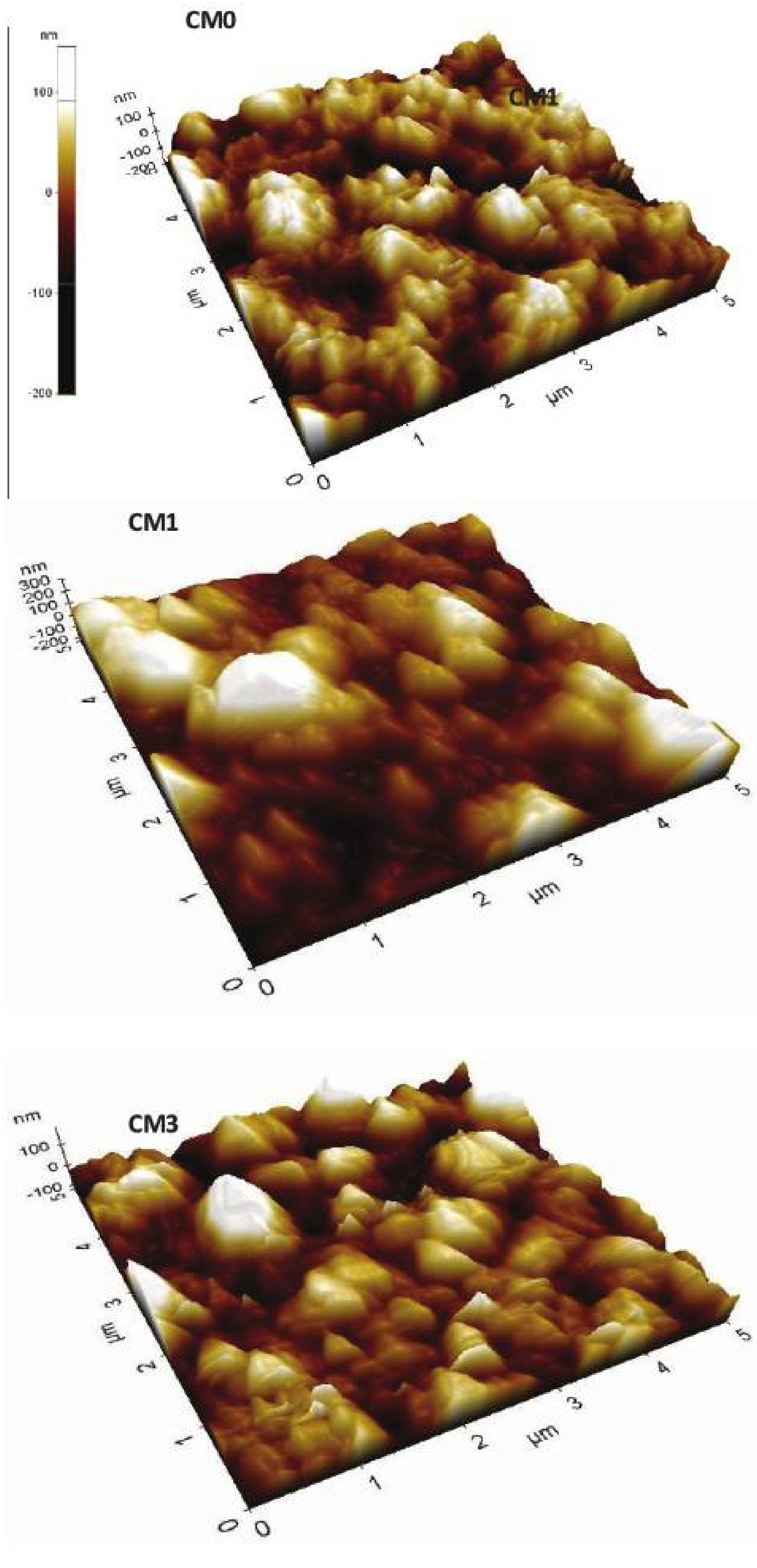


Figure 5. AFM images of CdS and CdS:Mn films

It was seen from Fig. 5, CM0 films show a surface morphology with cracks, pores and irregular aggregation of particles. There are randomly distributed mount type formations and regions with different height and width. Incorporation of Mn caused the formation of larger clusters with decreasing number of cracks for CM1 films. However, mount type formations are returned for CM3 films and together with increasing number of cracks and pores. Also, roughness values of the films are given in Table 2, show that all films have an average roughness value below 75 nm and sample CM3 has the lowest roughness value.

A four-probe set-up has been used to determine the electrical resistivity of annealed CdS and CdS:Mn films. The electrical resistivity values for samples CM0, CM1 and CM3 are given in Table 2. Incorporation of Mn caused a decrease in resistivity values. The contacts in four-probe set up have planar form. So, surface effects become dominant on the resistivity values when compared to bulk crystalline structure. We think that good packing texture of CM1 films caused the surface mobility to increase which in turn decreased the resistivity.

Table 2: R_q, R_a and R_{pv} roughness and electrical resistivity values CdS and CdS:Mn films

Film	R_q (nm)	R_a (nm)	R_{pv} (nm)	ρ (Ωcm)
CM0	46.76	37.82	346.68	$4.8X10^5$
CM1	92.99	74.65	537.04	$5.5X10^4$
CM3	43.03	33.96	301.74	$3.3X10^5$

4. CONCLUSION

In this work, annealed CdS and CdS:Mn films have been produced by a low cost USP technique. This technique has also the advantage of producing thin films on large areas. Optical properties have been studied by spectroscopic ellipsometry and UV/VIS spectrophotometer. The thickness, refractive index and extinction coefficient values have been obtained by fitting the experimental spectroscopic data by using Cauchy model. CM0 film has an average refractive index value in all annealed films. CM1 films with low refractive index have been obtained while CM3 high after the Mn incorporation which are annealed at 500°C. Besides, extinction coefficient values of all films showed almost similar behavior. Band gap values of the annealed films have been determined by optical method. Mn incorporation increased the band gap values of CM1 films while decreased CM3 films. AFM images showed that in all films, CM1 have dense and tight surfaces. Nevertheless, CM3 films have the lowest R_a, R_q and R_{pv} roughness value. Decreased resistivity values have been determined after Mn incorporation. This is an indication of the probability of producing alternative window materials for solar cell with a low cost USP technique.

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REFERENCES

[1] J. Herrero, M.T. Gutierrez, C. Guillen, J.M. Dona, M.A. Martinez, A.M. Chaparro, R. Bayon, "Photovoltaic windows by chemical bath deposition", Thin Solid Films. 361/362 (2000) 28-33.

[2] P.N. Gibson, M.E. Ozsan, D. Lincot, P. Cowache, D. Summa, "Modelling of the structure of CdS thin films", Thin Solid Films. 361/362, 34-40 (2000).

[3] M. Kostoglou, N. Andritsos, A.J. Karabelas, "Progress towards modelling the CdS chemical bath deposition process", Thin Solid Films. 387, 115-117 (2001).

[4] S. Prabahar, M. Dhanam, "CdS thin films from two different chemical baths-structural and optical analysis", J. Crys. Growth. 285, 41–48 (2005).

[5] O. Vigil, O. Z. Angel, Y. Rodriguez, "Changes of the structural and optical properties of cubic CdS films on annealing in H_2 and air atmospheres", Semicond. Sci. Technol. 15, 259–262 (2005).

[6] B. S. Moon, J.H. Lee, Hakkee Jung, "Comparison of structural and optical properties of CdS thin films grown by CSVT, CBD and Sputtering Techniques", Thin Solid Films. 511/512, 299–303 (2006).

[7] J. Nishino, S. Chatani, Y. Uotani, Y. Nosaka, "Electrodeposition method for controlled formation of CdS films from aqueous solutions", J. Electroanal. Chem. 473, 217–222 (1999).

[8] A. Rmili, F. Ouachtari, A. Bouaoud, A. Louardi, T. Chtouki, B. Elidrissi, H. Erguig, "Structural, optical and electrical properties of Ni-doped CdS thin films prepared by spray pyrolysis", J Alloy and Compd. 557, 53–59 (2013).

[9] P. P. Sahay, R. K. Nath, S. Tewari, "Optical properties of thermally evaporated CdS thin films", Cryst. Res. Technol. 42, 275 – 280 (2007).

[10] D. Sreekantha Reddy, K. Narasimha Rao, K.R. Gunasekhar, N. Koteeswara Reddy, K. Siva Kumar, P. Sreedhara Reddy, "Annealing effect on structural and electrical properties of thermally evaporated $Cd_{1-x}Mn_xS$ nanocrystalline films", Mater. Res. Bull. 43, 3245–3251 (2008).

[11] C. Wang, H.M. Wang, Z.Y. Fang, "Influence of Mn doping on the microstructure and optical properties of CdS", J. Alloy. Compd. 486, 702–705 (2009).

[12] D. Sreekantha Reddy, K. Narasimha Rao, K.R. Gunasekhar,Y. D. Reddy, P. S. Reddy, "Synthesis and dc magnetic susceptibility of the diluted magnetic semiconducting $Cd_{1-x}Mn_xS$ nanocrystalline films", J. Alloy. Compd. 461, 34–38 (2008).

[13] Q. Wang, Z. Xu, L. Yue, W. Chen, "Characteristics and optical properties of $Cd_{1-x}MnxS$ nanorods prepared through hydrothermal route", Opt. Mater. 27, 453–458 (2004).

[14] Q. Pang, B.C. Guo, C.L. Yang, S.H. Yang, M.L. Gong, W.K. Ge, J.N. Wang, "$Cd_{1-x}Mn_xS$ quantum dots: new synthesis and characterization", J. Crys. Growth. 269, 213–217 (2004).

[15] P. Sudhagar, R. Sathyamoorthy, S. Chandramohan, S. Senthilarasu, S.H. Lee, "Synthesis of $Cd_{1-x}Mn_xS$ nanoclusters by surfactant-assisted method: Structural, optical and magnetic properties", Mater. Lett. 62, 2430–2433 (2008).

[16] B. Tripathi, F. Singh, D.K. Avasthi, D. Das, Y.K. Vijay, "Study of effects of Mn^{2+} in CdS nanocrystals", Phys. B. 400, 70–76 (2007).

[17] A.I. Savchuk, V.I. Fediv, A.G. Voloshchuk, T.A. Savchuk, Yu.Yu. Bacherikov, A. Perrone, "New approach to synthesis of semimagnetic semiconductor nanoparticles", Mater. Sci. Eng. C. 26, 809 – 812 (2006).

[18] B. Tripathi, F. Singh, D.K. Avasthi, A.K. Bhati, D. Das, Y.K. Vijay, "Structural, optical, electrical and positron annihilation studies of CdS:Fe system", J. Alloy Compd. 454, 97–101 (2008).

[19] R. Sathyamoorthya, P. Sudhagar, A. Balerna, C. Balasubramanian, S. Bellucci,A.I. Popov, K. Asokan, "Surfactant-assisted synthesis of $Cd_{1-x}Co_xS$ nanocluster alloys and their structural, optical and magnetic properties", J. Alloy Compd. 493, 240–245 (2010).

[20] Y. Kashiwaba, K. Isojima, K. Ohta, "Improvement in the efficiency of Cu-doped CdS/non-doped CdS photovoltaic cells fabricated by an all-vacuum process", Sol. Energy Mater. 75, 253-259 (2003).

[21] J. Ma, G. Tai, W. Guo, "Ultrasound-assisted microwave preparation of Ag-doped CdS nanoparticles", Ultrason. Sonochem. 17, 534-540, (2010).

[22] Y. Cui, C.M. Lieber, "Functional nanoscale electronic devices assembled using silicon nanowire building blocks", Science, 291, 851, (2001).

[23] I. Gur, N. A. Fromer, M. L. Geier, A. P. Alivisator, "Air-stable all-inorganic nanocrystal solar cells processed from solution", Science, 310, 46, (2005).

[24] H.G. Tompkins, E.A. Irene, "Handbook of Ellipsometry", William Andrew Publishing, Norwich NY, 2005.

[25] H. Fujiwara, "Spectroscopic Ellipsometry Principles and Applications", John Wiley & Sons Ltd, West Sussex, England, (2007).

[26] Khoshman J.M., Kordesch M.E., "Spectroscopic ellipsometry characterization of amorphous aluminum nitride and indium nitride thin films", *Physica Statatus Solidi*, C2(7): 2821-2827 (2005).

[27] Goyal D.K., Pribil G.K., Woollam J.A., Subramanian A., "Detection of ultrathin biological films using vacuum ultraviolet spectroscopic ellipsometry", *Material Science Engineer B.*, 149: 26-33 (2008).

[28] Z.G. Hu, G.S. Wang, Z.M. Huang, J.H. Chu, "Optical properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films using spectroscopic ellipsometry", Appl. Phys. 93, 3811–3815 (2003).

[29] Hiroyuki Fujiwara, "Spectroscopic Ellipsometry:Principles and Applications", John Wiley & Sons, England, (2007).

[30] J.M. Khoshman, M.E. Kordesch, J.M. Khoshman, M.E. Kordesch, "Optical characterization of sputtered amorphous aluminum nitride thin films by spectroscopic ellipsometry", J. Non-Cryst. Solids 351, 3334–3340 (2005).

[31] P. Rajı, C. Sanjeevıraja, K. Ramachandran, "Thermal and structural properties of spray pyrolysed CdS thin film", Bull. Mater. Sci. 28, 233–238 (2005).